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LUBRICATING COMPOSITION

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The present invention relates to improvements in lubricating oils and more especially to oils of high quality and capable of withstanding high pressure and generally severe service. The present composition will be fully described in the following specification.

During the last several years leaded lubricating oils have found general application but there are objections to the present compounds which limit their use considerably. One is the instability of the lead oleate which is generally used particularly in high grade base oils. The compound is not freely soluble in high grade base oils, such as the distillates or bright stocks derived from wax bearing crudes. At ordinary temperatures and on standing for a relatively short time the compound settles out of the oil in a thick sludge. For this reason the leaded compounds must be made up from relatively low grade base oils. The distillate stocks used are oils of relatively low viscosity index, such as oils derived from wax free crudes which in general have viscosity indices below 50 on the scale devised by Davis and Dean, Chem. and Met. Engineering 36-618 (1929). Heavy residual oils such as black oils, rich in tarry or asphaltic substances (which sometimes show higher viscosity indices than 50) are used for leaded lubricants, but the high grade residuals such as bright stocks or dewaxed bright stocks are not available because of their failure to hold the lead in a stable form.

It is highly desirable to make use of the better grade of base oils, specifically the distillates and residuals of waxy crudes for leaded compounds in order to obtain a better viscosity-temperature curve and resistance to oxidation and sludge formation which is characteristic of these oils.

The present invention deals with the leaded compound produced from a high grade oil, for example, distillates having a viscosity index above 60, or even above 80 or 90 and residuals free from asphalt having viscosity indices above 80, 85, or even 90. It is thus possible by the present method to produce stable, light-colored, clean, transparent oils containing lead in effective quantities from oils of Pennsylvania quality or even better such as hydrogenated petroleum oils, high grade oils produced by solvent extraction processes, and even the synthetic oils produced by condensation of cracked or dehydrogenated wax and the like, either alone or condensed with aromatic hydrocarbons.

In order to make the leaded compound soluble and stable, acids others than oleic are used; for example, naphthenic and sulfonic acids are the

most desirable. The naphthenic acids are of the type obtained either from Russian, Rumanian or certain American crudes, especially those obtained from California. These acids are obtained as mixtures and have average molecular weights of about 250 or higher. They should be carefully refined so as to separate as completely as possible the oily non-acid constituents and in this condition they are light lemon-yellow in color. The sulphonic acids are preferably those obtained by the refining treatment of lubricating oils with fuming or other highly concentrated sulfuric acid. The acids are conveniently obtained as a by-product in the manufacture of "white" oil for medicinal and technical purposes and are the so-called Mohogany acids which remain largely in the oil after the acid treatment.

In producing the leaded compounds of these acids the requisite amount of lead oxide, litharge, is added to the acids and the temperature is raised to effect the combination. The proportion of lead is, say, 30% where the naphthenate is used, and, say, 18% for the sulphonate, and it is preferred to make the lead compound from the oxide to other lead compounds such as the salts, although these latter can be used. For example, the lead compound may be made by reaction of sodium naphthenate or sodium sulphonate with lead nitrate or other suitable salt. When the compound has been produced it is incorporated in the oil without difficulty by suitably raising the temperature while stirring vigorously.

The base stock preferred is, as stated above, an oil of high viscosity index, of good color and otherwise well refined. Its viscosity may vary considerably, depending upon the service to which the oil is destined. For some purposes the viscosity may be from 50 or 60 seconds Saybolt at 210° F., to 80 or 90, but for gear and transmission oils higher viscosities are desirable, say above 110 or 120 at 210° F., and they may be as high as 200, 250 or more for particularly heavy duty.

The leaded compound is ordinarily added in a proportion below about 10% of the oil. For example, within the range of 5-15% or, expressed in terms of lead, for most purposes 2-3% gives satisfactory results.

To the above blend may be added relatively small amounts of oil-soluble substances rich in sulfur. Various materials may be used for different purposes but synthetics are preferred since they can be produced with good color and odor. The synthetics which are used are, of course, organic compounds soluble in the oil, at least to

such an extent as to furnish $\frac{1}{2}$ to 5% of sulfur and they should be of high enough molecular weight and boiling point so as not to be lost by evaporation at the temperature of use. The compounds are also preferably of the type known as corrosive. This does not mean that they corrode bearings or gears to any appreciable extent but merely that they rapidly tarnish or discolor a bright strip of copper which is allowed to stand in the liquid for several hours at 212° F. according to the A. S. T. M. corrosion test.

For this purpose sulfurized animal, vegetable and marine oils are useful and they may be prepared by various methods, for example, reaction of elemental sulfur on the fatty oils. Other suitable corrosive sulfur-bearing synthetics may be produced by the reaction of inorganic sulfur-bearing compounds on halogenated aliphatic hydrocarbons. For example, the sulfides, polysulfides and hydro-sulfides of alkali and alkaline earth metals may be caused to react with chlorinated hydrocarbons, for example, paraffin wax, at temperatures of about 200° to 300° F. The sulfur appears to replace the chlorine at these temperatures and if sufficient time is allowed, the substitution may be complete. It is sometimes desirable, however, to replace the sulfur only partially so that both sulfur and chlorine may be present together, say in equal quantities, or either one or the other may be in excess. The synthetic, by whatever method it may be produced, is added to the oil so as to provide sulfur in proportion of about $\frac{1}{2}$ to 5% by weight.

The oils produced by the above methods are extremely stable and show no tendency to separate a lead sludge. They may be of extremely high viscosity index, depending upon the base stock, and even with high viscosity index the high degree of stability persists. They may be of light color if well refined ingredients are used in their preparation and the composition containing the lead compound and corrosive sulfur is of particular advantage since it is capable of withstanding extremely high bearing pressures under conditions of a rapidly applied load. As examples of the present compounds the following may be considered:

Example 1.—To a suitable base oil 10% of a lead compound produced from naphthenic acid is added. The lead compound is produced by heating approximately 25 pounds of a lead oxide with 50 pounds of naphthenic acids having an acid value of 223 and derived from a California crude. To this compound is then added 3% of a synthetic containing corrosive sulfur. The synthetic is produced by treating pine oil with sulfur at a temperature of 200° C. The inspection of the base oil (I), the blend before addition of the synthetic sulfur compound (II), and of the blend after such sulfur compound has been added (III) are given below:

	I	II	III
Gravity.....	27.7	24.6	24.6
Viscosity at 210° F.....	86	86	93
Viscosity at 100° F.....	912	912	978
Viscosity index.....	99	99	105
Pour point.....	25° F.	25° F.	25° F.
Color.....	1 $\frac{1}{4}$	1 $\frac{1}{4}$	1
Percent sulfur.....	.021	.022	1.61

The base oil (I) showed a load bearing capacity of 5 wts. when tested on the well-known Mougey machine and 3 wts. on the Almen machine. The leaded blend (II) gave bearing capacities of 8-10 wts. and 2 wts. respectively on the two machines,

and the blend containing the sulfur compound (III) showed values of 25 wts. and 15 wts. (capacity loads) respectively. It will be noted that the lead-sulfur compound is especially effective on the Almen machine which shows the effect of a rapidly applied load.

The blended oils are found to be of high stability; for example, no settling is noticed after several weeks standing.

Similar results were obtained using a sulfurized compound produced from lard oil by the action of sulfuryl chloride.

Example 2.—In another similar composition a hydrogenated oil having a viscosity of 102 at 210° F. and a Viscosity Index of 90 is incorporated with 10% of lead sulfonate and 5% of a corrosive synthetic produced by refluxing paraffin, which had been chlorinated to the extent of 20%, with sodium polysulfide. The synthetic contained about equal amounts of sulfur and chlorine. The inspection of the base oil (I) and the final product (II) are as follows:

	I	II
Gravity.....	26.0	23.5
Viscosity at 210° F.....	102	105
Viscosity at 100° F.....	1,380	1,450
Viscosity index.....	90	90
Pour point.....	15	15
Color.....	2	1 $\frac{1}{2}$
Percent sulfur.....	0.19	1.09

In load bearing tests the base oil successfully stood a bearing pressure of 5 wts. on the Mougey machine and 3 wts. on the Almen machine, respectively, while the blend showed increased values of 25 wts. and 15 wts. respectively.

Example 3.—As a third example, the base oil comprises a synthetic hydrocarbon lubricating oil produced by aluminum chloride condensation of cracked paraffin wax. To this base 10% of lead naphthenate is added with 4% of sulfurized pine oil.

The inspection of the base oil (I) and the blend (II) are as follows:

	I	II
Gravity.....	27.6	24.5
Viscosity at 210° F.....	120	122
Viscosity at 100° F.....	1,390	1,410
Viscosity index.....	110	110
Pour point.....	0° F.	5° F.
Color.....	2R	1R
Percent sulfur.....	—	1.20

In the above examples reference has been made to Mougey and Almen tests. These have been described in detail in Nat. Pt. News, Nov. 11, 1931, p. 47, and Nov. 16, 1932, p. 39; and the tests were conducted in strict accordance with the author's methods.

Other examples might be readily multiplied but those given above bring out the important features, especially the stability of the oil and the increased load bearing capacities of the compounds, particularly when containing small amounts of corrosive sulfur. Other compounds can be readily made by using the various ingredients mentioned hereinabove without departing from the spirit of the invention.

The invention is not to be limited to any particular lead compound nor to any particular base stock or in fact to any particular substance of sulfur, but only to the following claims in which it is desired to claim all novelty inherent in the invention.

I claim:

1. An improved lubricating composition of high stability, comprising as a base stock a lubricating oil of high viscosity index containing in solution both a small quantity of a leaded compound of an acid selected from the class of naphthenic and sulfonic acids and an oil soluble substance rich in sulphur. 5
2. An improved lubricating composition comprising a major proportion of lubricating oil base characterized by a viscosity index above 60 and containing in solution both a lead compound soluble therein selected from the class of naphthenate and sulphonate and an oil soluble substance rich in corrosive sulphur. 10
3. Composition according to claim 2 in which the lead compound comprises lead naphthenate and the sulphur rich material is selected from the class of sulphurized animal, vegetable and marine oils. 15
4. Composition according to claim 2 in which the lead compound comprises lead naphthenate and the sulphur rich material is a sulphurized vegetable oil. 20
5. Composition according to claim 2 in which the lead compound comprises lead naphthenate and the sulphur rich material comprises sulphurized pine oil. 25
6. Composition according to claim 2 in which the lead compound comprises lead sulphonate and the sulphur rich material is selected from the class of sulphurized animal, vegetable and marine oils. 30
7. Composition according to claim 2 in which the lead compound comprises lead sulphonate and the sulphur rich material is a sulphurized vegetable oil. 35
8. Composition according to claim 2 in which the lead compound comprises lead sulphonate and the sulphur rich material comprises sulphurized pine oil. 40
9. An improved lubricating oil comprising a major proportion of a base stock characterized by a viscosity index above 80 and containing in solution both a soluble lead compound selected from the class of naphthenates and sulphonates and an oil soluble substance rich in sulphur and selected from the group of sulphurized animal, vegetable and marine oils of the corrosive type. 45
10. An improved lubricating oil comprising a major proportion of a base stock characterized by a viscosity index above 90 and containing in solution both a soluble lead compound selected from the class of naphthenate and sulphonate, and an oil soluble substance rich in sulphur selected from the class of sulphurized animal, vegetable and marine oils. 50
11. Composition according to claim 10 in which the lead compound is lead naphthenate and the sulphur compound comprises a sulphurized vegetable oil. 10
12. Composition of matter according to claim 10 in which the lead compound is lead naphthenate and the sulphur compound is a sulphurized pine oil. 15
13. Composition according to claim 2 in which said oil soluble substance rich in corrosive sulphur contains halogen. 15
14. Composition according to claim 9 in which said sulphurized oil contains chlorine. 20
15. Composition according to claim 9 in which said sulphurized oil contains sulphur and chlorine in equal quantities. 20
16. A composition according to claim 2 in which the proportion of lead is from about 2% to 3% and of sulfur is from about $\frac{1}{2}$ to 5%. 25
17. A composition according to claim 2 in which the proportion of lead is from about 0.9% to 4.5% and of sulfur is from about $\frac{1}{2}$ to 5%. 25
18. An improved lubricating composition of high stability, comprising as a base stock a lubricating oil of high viscosity index containing in solution both a small quantity of a leaded compound of an acid selected from the class of naphthenic and sulfonic acids and a sulfurized fatty oil of the non-drying type. 30
19. An improved lubricating composition of high stability comprising as a base stock a lubricating oil of high viscosity index containing in solution both a small quantity of a leaded compound of an acid selected from the class of naphthenic and sulfonic acids and a sulfurized non-drying fatty oil of the corrosive type. 35
20. An improved lubricating oil composition of high stability comprising as a base stock a lubricating oil of high viscosity index containing in solution both a small quantity of a lead compound of an acid selected from the class of naphthenic and sulfonic acids and sulfurized lard oil. 45

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